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ABSTRACTS
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(Pages refer to the Japanese originals of this volume unless otherwise noted.)

Blätteralkohol. VI. Mitteilung(1)

Über die katalytische 1 Mol. Hydrierung von Hexin-3-ol-1 mittels Platinoxyd.

(SS. 625～628)

Von Sankiti Takei and Minoru Ôno.

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Eingegangen am 13. März. 1942.)

Unseren früheren Arbeiten(2) zufolge kann man bei der katalytischen 1 Mol. Hydrierung von Hexin-3-ol-1 mittels Pd-$BaSO_4$ je nach den Temperaturbedingungen Blätteralkohol (*trans*-Hexen-3-ol-1) oder sein Isomer (*cis*-Hexen-3-ol-1) gewinnen. Es war für uns nun von Interesse, ob man das gleiche Ergebnis erzielen könnte, wenn man in dieser Reaktion statt Pd-$BaSO_4$ als Katalysator PtO_2 verwendet. Zunächst haben wir die 1 Mol. Hydrierung des Hexin-3-ol-1 mittels PtO_2 bei −19° durchgeführt; dabei wurde ausser dem Blätteralkohol (ca. 40%) ein neues Hexenol (ca. 60%) gewonnen. Bei Anwendung einer höheren Reaktionstemperatur (60°) ergab sich aber nur das neue Hexenol.

Das Hexenol riecht sehr ähnlich wie der Blätteralkohol und liefert Allophanat vom Schmp. 129°, Anthrachinon-β-carbonsäure-ester vom Schmp. 61° und 3,5-Dinitrobenzoesäure-ester vom Schmp. 37°. Bei der $KMnO_4$-oxydation wurde das Hexenol quantitativ in Essigsäure und Bernsteinsäure gespaltet.

Auf Grund dieser Ergebnisse kann man feststellen, dass das Hexin-3-ol-1 durch katalytische 1 Mol. Hydrierung mittels PtO_2 bei tiefer Temperatur in *trans*-Hexen-3-ol-1 und bei höherer in *Hexen*-4-*ol*-1 übergeht.

Schrifttum.

(1) V. Mitteil: J. Agr. Chem. Soc. Japan, 18 (1942), 110.
(2) IV. Mitteil: J. Agr. Chem. Soc. Japan., 16 (1940), 772.

Studies on the Yeasts Found in "Miso."

(pp. 629～641)

By Masatoshi MOGI.

(The Brewing Laboratory, Noda Syôyû Co., Ltd., Tiba-ken;
Received February 16, 1942.)

Studies on Methionine and its Derivatives. (V).
Studies on Utilization of Methionine.

(1) On the Nutritive Value of Modified Milk Powders (Preliminary Experiment.)

(2) Use of Methionine in the Preparation of Biscuit (Preliminary Experiment.)

(pp. 624～650)

By Yoshio TSUCHIYA and Toshi ISOBE.

(S. Suzuki and Co., Ltd; Received March 24, 1942.)

Studies on Grape Seed Oil.

(pp. 651～654)

By Kunio ISHIMARU.

(The Institute of Physical and Chemical Research; Received March 11, 1942.)

Untersuchungen über die Beziehungen von Bataten zur Alkoholproduktion. (V.)

(SS. 655～664)

Von Y. TAKEDA, K. SUEMATU und M. UTIKOSI.

(The Institute on Chemical Industry, Government-General of Taiwan, Nippon:
Received March 9, 1942.)

Dehalogenations of the Halogenated Sugar Alcohols. (Part V.)

The Structure of Bouchardt's Dichlorodulcitol.

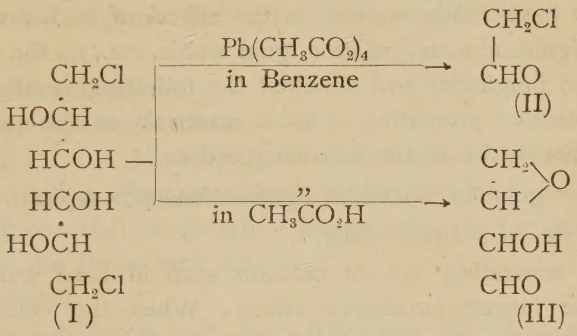
(pp. 665～668)

By Yasuji HAMAMURA.

(Kyoto Sericultural College; Received March 2, 1942.)

The author tried to prepare 1,6-diiododulcitol in the same manner as in the cases of mannitol and sorbitol. The attempt, however, could not succeed because dulcitol does not act on tritylchloride.

The author recollected that Bouchardt had prepared(1) dichlordulcitol (I) from dulcitol and conc. hydrochloric acid, and also dichlormannitol in the similar way. The position of chlorine atoms of the latter has already been determined as 1 and 6 of mannitol by F. Micheel,(2) but the former has not yet been determined. The author infers the positions of these chlorine atoms to be also 1 and 6 from the experiments, as follows :—



(II) Monochloracetaldehyde as dinitrophenylhydrazone, m. p. 154∼5°C, N% 22.24 (calc. N% 22.66).

(III) Anhydrothreose as *p*-nitrophenylosazone (under reexamination) decomposed over 300°C, C% 51.73, H% 4.12 N% 22.30 (calc. C% 51.73, H% 3.78, N% 22.70).

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(1) Bouchardt: Am. Chem. Phs., **4** (1872), 27, 145, 168.
(2) F. Micheel: Ann., **496** (1932), 77.

On the Chemical Studies of the Baggasse Pulp. (10).

(pp. 669∼672)

By T. TADOKORO and M. NISHIDA.
(Hokkaido Imperial University; Received March 19, 1942.)

Distribution of Ascorbic Acid in Plant Materials of North Nippon. I.

(pp. 673∼689)

By Hisayosi IWATA, Kyo ITO, and Goro MAESAWA.
(Morioka Imperial College of Agriculture and Forestry; Received January 16, 1942.)

Chemical Studies on Agricultural Insecticides. (Part 5).

On the Effect of Protective Colloids on the Dispersion of Insecticides and Fungicides in Water.

(pp 690∼696)

By Chiyoka MOURI and Hiroshi NORIMATSU.

(Central Laboratory, South Manchuria Railway Company, Dairen;
Received March 20, 1942.)

The authors have made studies on the effects of such protective colloids as saponin, sodium ligninsulfonate, gelatine, gum arabic, etc., on the colloidal dispersion of insecticides and fungicides and obtained the following results.

1. The protective properties of these materials on the coagulation of congo rubin sol are shown to be in the following order:

gelatine > sodium ligninsulfonate > saponin.

Gum arabic has shown a small effect.

2. On the separating out of calcium soap in hard water, sodium ligninsulfonate has the largest protective effect. When the concentration of soap (sodium palmitate) in hard water of 30°, 50°, 100°, or 140° (in German degree), is in every case 0.25%, the sufficient concentration of the sulfonate to give the protective effect in each of the above mixtures is 0.0075%, 0.025%, 0.05%, or 0.1%, respectively.

3. On the dispersion of kerosene miscible oil emulsion in hard water corresponding to 70°, 100°, or 140, containing a soap (sodium palmitate) concentration of 0.25%, sodium ligninsulfonate is effective at concentrations of 0.05%, 0.1%, or 0.1∼0.25%, respectively.

4. To prevent separating out of copper soaps, sodium ligninsulfonate has been found most effective while gum arabic shows a moderate effect. When the concentration of copper soap (cupric palmitate) is 0.5%, sodium ligninsulfonate at the concentration of 0.05% is sufficient.

5. To prevent the separation of cupric hydroxide in water, corresponding to the concentration of 0.1% of $Cu(OH)_2$, sodium ligninsulfonate is most effective and is sufficient when its concentration is 0.1%.

On the Manufacture of Acetone and Butanol by Fermentation. (2).

(pp. 697∼706)

By H. OKEDA, N. SOWA, A. WATABE, and Y. HASHIMOTO.

(Nippon Soda Co., Ltd.;
Received March 16, 1942.)

Untersuchungen über die Verwitterung der Eruptivgesteine. VIII.

Neue Farbenreaktionen zum Nachweis der Tonmineralien.

(SS. 707～713)

Von Mituru HARADA.

(Landwirtschaftliche Hochschule uz Tottori.
Eingegangen am 16. 3. 1942.)

Der Verfasser hat folgende Farbenreaktionen zum Nachweis der Tonmineralien gefunden.

I. Nachweis von Montmorillonit

(a) Paraphenylendiamin-Methode

Versetzt man 1 g der Montmorillonit enthaltenden Probe mit 5 cc 2%iger Boraxlösung und 0,02 g Paraphenylendiamin-hydrochlorid (oder Paraphenylendiamin), wird die Probe tiefblau gefärbt. Säuert man das Gemisch mit verdünnter Salzsäure an, färbt die Probe sich rot.

(b) Metol-Methode

Versetzt man 1 g Probe mit 5 cc 0,5% iger Metollösung, 5 cc 10%iger Natriumacetatlösung und 0,01 g MnO_2, wird der Montmorillonit tiefblau gefärbt.

(c) Neue Benzidin-Methode

Die Anwesenheit von Montmorillonit kann man durch die tiefe Blaufärbung erkennen, die auf Zugabe von Ammoniakwasser und Benzidinhydrochloridlösung (oder Benzidinlösung) zur Probe entsteht. Diese Reaktion ist sehr empfindlich. Ohne Ammoniak wird durch MnO_2 in der Probe das Gemisch auch blau gefärbt.

II. Nachweis von Halloysit und Kaolinit.

MnO_2-Benzidin-Methode

Wenn man 1 g Probe mit 0,01 g MnO_2 und 5 cc zitronensaurer Benzidinlösung (0,1 g Benzidinhydrochlorid oder Benzidin, 10 g Zitronensäure, 100 cc Wasser) versetzt und vermischt, werden Halloysit und Kaolinit violett gefärbt. Der Nachweis des Kaolinits wird nach der Beseitigung des Halloysits gemacht: die Probe wird mit konzentrierter Salzsäure erhitzt, filtriert, bis zum Verschwinden der sauren Reaktion ausgewaschen, und dann wird der Rückstand, der Komplex B enthält, mit MnO_2 und der Benzidinlösung behandelt. Nach der Salzsäurebehandlung fällt diese Reaktion bei der nur Halloysit enthaltenden Probe negativ aus.

Der Gehalt an Komplex A_1, A_2⁽¹⁾ und B, das Mol-Verhältnis von SiO_2/R_2O_3 und die Farbenreaktion der Tonmineralien in verschiedenen Böden aus Eruptivgesteinen sind in der folgenden Tabelle dargestellt. Der Boden, dessen Komplex B das Verhältnis von SiO_2/R_2O_3 ca. 3 hat, zeigt die Farbenreaktion von Montmorillonit und Kaolinit. Komplex B, der das Mol-Verhältnis von ca. 2 hat, zeigt die Kaolinit-Reaktion. Der Boden, der an Komplex A_2 reich ist, zeigt die Halloysit-Reaktion deutlich. Der nur Komplex A_1 enthaltende Boden hat keine Farbenreaktion.

Komplex A_1, A_2, B und Tonmineralien in den Böden aus Eruptivgesteinen.

(O = Oberhorizont, M = Mittelhorizont, U = Unterhorizont
Mo = Montmorillonit, Ha = Halloysit, Ka = Kaolinit)

		Komplex A_1 (%)	Komplex A_2		Komplex B		Tonmineralien
			SiO_2 + R_2O_3 (%)	$\frac{SiO_2}{R_2O_3}$	SiO_2 + R_2O_3 (%)	$\frac{SiO_2}{R_2O_3}$	
Granitboden	(1)	0,40	0,16	2,18	27,64	3,36	Mo, Ka
	(2)	1,42	11,93	1,94	20,52	1,84	Ha, Ka
	(3)	1,75	20,50	2,20	24,16	1,96	Ha, Ka
Quarztrachytboden (1)	O	0,22	7,53	2,39	26,57	2,84	Mo, Ka, Ha
	M	0,26	6,96	1,87	29,07	3,08	Mo, Ka, Ha
	U	0,38	9,02	2,43	11,83	3,46	Mo, Ka, Ha
Quarztrachytboden (2)	O	0,45	10,00	2,01	15,84	2,06	Ha, Ka
	U	0,50	14,75	1,97	18,74	2,29	Ha, Ka
Dioritboden		1,36	16,59	2,22	15,10	1,87	Ha, Ka
Basaltboden (1)	O	1,20	44,01	1,78	16,30	1,89	Ha, Ka
	M	1,50	53,20	1,95	5,66	1,82	Ha, Ka
	U	2,03	65,64	2,05	4,41	1,84	Ha, Ka
Basaltboden (2)	O	2,43	8,43	1,91	46,64	1,95	Ha, Ka
	M	2,00	17,53	1,91	39,14	1,90	Ha, Ka
	U	2,05	18,32	1,89	1,07	5,11	Ha, (Mo)
Basaltboden (3)	O	1,85	25,15	1,92	15,03	1,88	Ha, Ka
	M	2,26	35,08	1,92	12,53	1,90	Ha, Ra
	U	2,40	25,51	1,81	6,04	2,61	Ha, Ka, (Mo)
Augitandesitboden	O	1,88	44,40	1,73	12,35	2,02	Ha, Ka
	U	2,26	62,96	1,95	2,97	1,64	Ha
Hornblendeandesitboden	O	14,64	8,18	1,79	1,39	2,22	Ha
	U	1,83	1,85	2,37	0,15	2,05	Ha
Vulkanischer Boden	O	2,35	14,03	1,99	7,26	1,96	Ha, Ka
	U	27,22	1,22	2,16	—	—	—

Schrifttum.

(1) M. Harada: Bulletin of Agr. Chem. Soc. of Japan, **16** (1940), 77.

Studies on the Components of the Bark of Rhamnus japonica (VII).

The Chemical Characters of the Lactone Ring of α-Sorinin and its Derivatives.

(pp. 714~716)

By Zirô NIKUNI.

(Agr. Chem. Laboratory, Tokyo Imp. Univ.; Received March 23, 1942.)

The lactone equivalents of α-sorinin and its derivatives are determined according to Fujita's method (J. of Pharm. Soc. Japan. **55**, 291, 1935).

This method is carried out as follows: An excess amount of caustic alkaline solution is added to the sample and heated on the water-bath, and then back titrated with sulphuric acid solution. Thus the saponification equivalent is determined. Then the excess amount of sulphuric acid is added and the whole mixture is heated to close the lactone ring, and the sulphuric acid is back titrated with alkaline. The lactone equivalent is derived from the following equation:—

$$\text{The lactone equivalent} = \frac{10{,}000 \times P}{n},$$

where P is grams of the sample and n is volume (cc) of 0.1 N sulphuric acid solution.

The results are summarized in the following table.

Sample (g)	0.1 N NaOH (cc)	0.1 N H_2SO_4 (cc)	Saponification equivalent	Lactone equivalent
(1) Dimethyl-α-sorigenin				
(a) 0.0186	0.65	0.65	286	286
(b) 0.0467	1.67	1.90	279	245
as $C_{15}H_{14}O_5$			274	274
(2) α-Sorigenin				
(a) 0.0356	1.39	0.15	256	2373
(b) 0.0254	1.05	0.11	241	2309
as $C_{13}H_{10}O_5$			246	246
(3) α-Sorinin				
(a) 0.0272	0.36	0.41	755	663
(b) 0.1090	1.71	1.46	626	733
as $C_{24}H_{28}O_{14}$			530	530
(4) Diacetyl-α-sorigenin				
0.0201	1.85	0.18	108	1116
as $C_{13}H_8O_5(CH_3CO)_2$			110	330
(5) Monomethyl-α-sorigenin				
(a) 0.0377	1.39	0.56	271	673
(b) 0.0320	1.00	0.38	320	842
as $C_{14}H_{12}O_5$			260	260
(6) Phthalid				
0.1006	7.56	7.00	136	143
as $C_8H_6O_2$			134	134
(7) Santonin				
0.0540	2.36	2.32	228	232
as $C_{15}H_{18}O_3$			246	246

The character of the lactone ring depends upon the hydroxyl-groups of these compounds. For instance, the lactone ring of α-sorigenin, which has two free hydroxyl-groups, is opened very easily by dilute alkaline solution even at room temperature. And the ring closes again by addition of dilute acid solution. The ring opens too easily by alkaline solution so that the lactone equivalent becomes too large.

The lactone rings of α-sorinin and monomethyl-α-sorigenin, which have one hydroxyl-group, open and close more difficultly than that of α-sorigenin.

On the other hand the ring of dimethyl-α-sorigenin, which has no free hydroxyl-group, opens and closes only by alkaline and acid of moderate concentration, and at high temperature.

The author expresses his sincere thanks to Prof. B. SUZUKI for his kind guidance throughout this work.

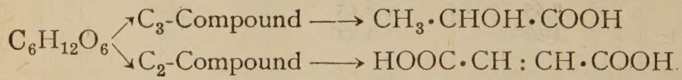
Studies on the Acid Fermentation by Rhizopus Species. (Part II.)

(pp. 717∼718)

By Kinichirô SAKAGUCHI, Toshinobu ASAI, and Hirohisa MUNEKATA.

(Agricultural Chemical Laboratory, Tokyo Imperial University; Received March 9, 1942.)

In the previous paper the authors assumed the following scheme for lactic or fumaric acid formation by Rhizopus species:



$$C_6H_{12}O_6\begin{array}{l}\nearrow C_3\text{-Compound} \longrightarrow CH_3\cdot CHOH\cdot COOH\\ \searrow C_2\text{-Compound} \longrightarrow HOOC\cdot CH : CH\cdot COOH\end{array}$$

Pyruvic acid may be regarded as one of the most probable precoursers to lactic acid as well as to fumaric acid, where the direct precourser to the former or the intermediate C_2-compound as above mentioned, may be derived through the carboxylatic fission of pyruvic acid. This experiment has been carried out to investigate the metabolic products from Na-pyruvate by both the fumaric and lactic acids formers, Rh. G 34 and Rh. G 36, with the following results:—

1) Lactic acid has not been found in the fermented liquids of both species. While remarkable quantities of fumaric acid have been formed in either case.

2) The production of ethyl alcohol only by the fumaric acid former, Rh. G 34 was recognized.

3) Acetic and formic acids were formed abundantly by both species. The ratio acetic/formic was found to be approximately 2∼2.5 : 1. The breakdown of the pyruvate may therefore be supposed to take place according to the following equation:—

$$CH_3\cdot CO\cdot COOH + H_2O \longrightarrow CH_3\cdot COOH + H\cdot COOH$$